



# Current and Future Calibration and Validation Activities, Advanced Planning, and Future Round Robins: *Will We Be Ready for the Next Mission?*

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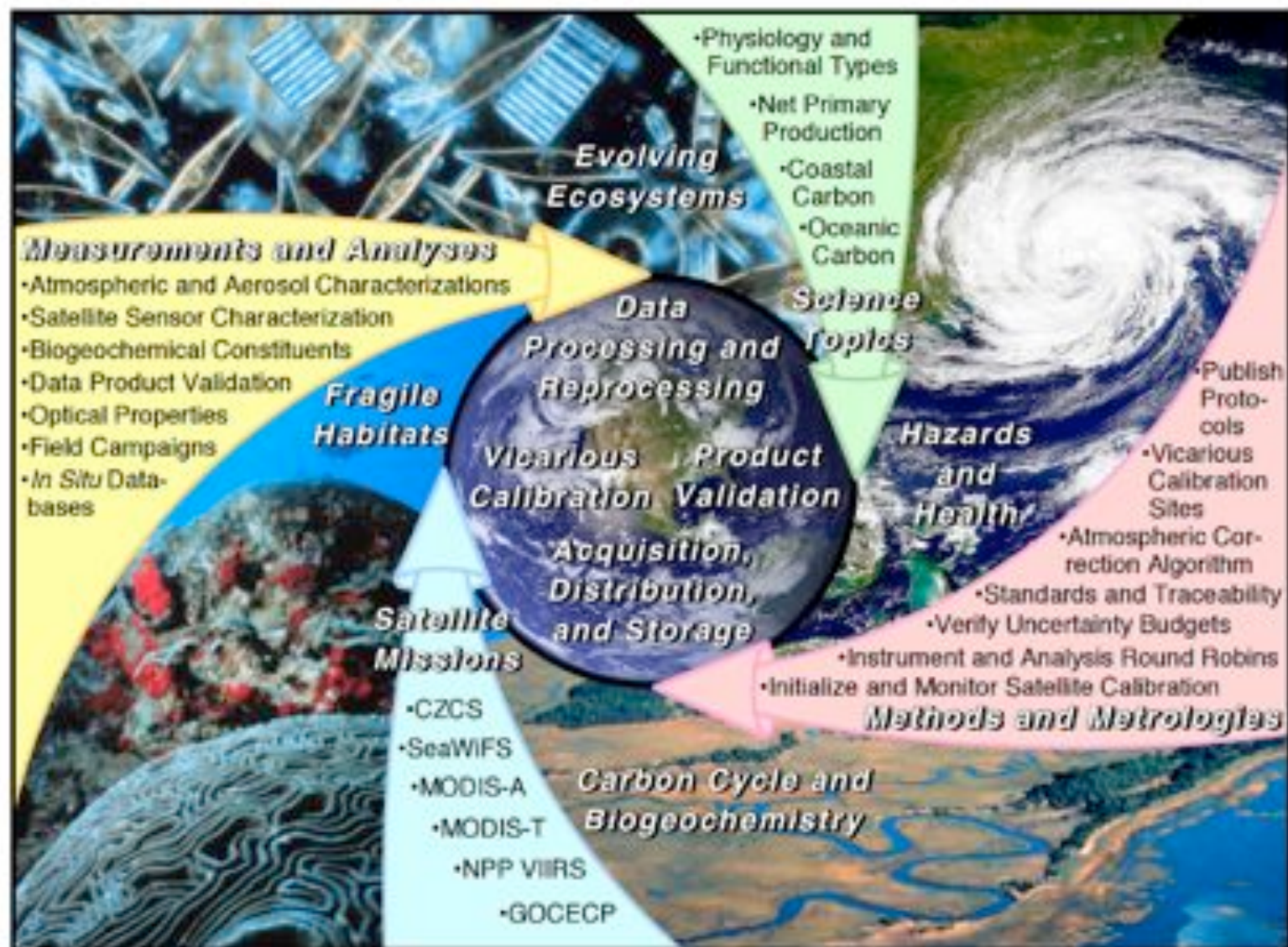
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## The Synergism of the Advanced Science Plan and the Calibration and Validation Plan







## The Calibration and Validation Plan: A New Paradigm For Ocean Color



All elements are seen to be interdependent, that is, they connect like puzzle pieces, and when they are properly joined, a comprehensive capability for the entire activity emerges. A horizontal organizational scheme is anticipated and the entire enterprise is split into two components of equal stature: calibration and validation plus satellite data processing. For the former, **all of the needed disciplines are included at the same priority level with no preconceived notions of resource allocations.**





## The Calibration and Validation Plan: GSFC Scientists and Tasks



In addition to incorporating reviewer comments into a revised plan, **core personnel** (blue and red) have met to discuss a follow-on implementation plan. As part of the latter, the core scientists have agreed to who will be the primary and secondary representatives for every element. Emphasis was placed on ensuring **the connecting-core** (green and yellow) elements, which are competed or contracted, respectively, had scientists with an established expertise or visibility in the ocean color community.



## Short- and Long-Term Task Planning by the Calibration and Validation Office

The tasks being planned by the Calibration and Validation Office include:

1. Publishing the final version of the Calibration and Validation Plan.
2. Producing the Implementation Plan (which will be posted for public review).
3. Updating The Protocols using a common format and organizational scheme (which have been agreed to). Principal leads for each current and anticipated methodology are being identified. All protocols will be evaluated according to open ocean, coastal waters, and estuarine requirements. Some missing protocols need to be resolved by community consensus (e.g., primary productivity).
4. Identifying what workshops are needed: a) updating The Protocols (in particular, resolving missing methods), b) round robins (HPLC and IOPs), c) verifying uncertainties (IOPs), d) reducing uncertainties (a Web-based AOP data processor), and e) evaluating alternatives and achieving consensus on important tasks (vicarious calibration). **Plus, there will be others from the OCRT Meeting.**
5. Understanding the requirements for future round robins by engaging in smaller test-beds (small IOP intercomparisons are being planned for this year).
6. Making sure existing round robins provide preliminary assessments for logical follow ons (particulate absorption, plus the spectrophotometric and fluorometric determination of the chlorophyll *a* concentration are a part of SeaHARRE-4).





## The Premise and Utility of Round Robins—In Particular Those Based on Natural Samples (SeaHARRE)

The premise of a round robin is *all participants use a validated method, which are equally capable of estimating a true result for each “sample,” and each sample is analyzed no differently than any other normally analyzed by the method.*

The result from each method is expected to be close to the truth (which is frequently unknown), and the dispersion of the results will be equally expressed above and below the true value. A validated method has no inherent biases, because if one existed it would have been removed by the validation process. The computation of the accuracy (or uncertainty) for each method is based on computing the difference of each result from the truth (usually the average of all data) for each product.

*Accuracy* estimates how close the result is to the true value while *precision* is an estimate of how exactly the result is determined independently of any true value.

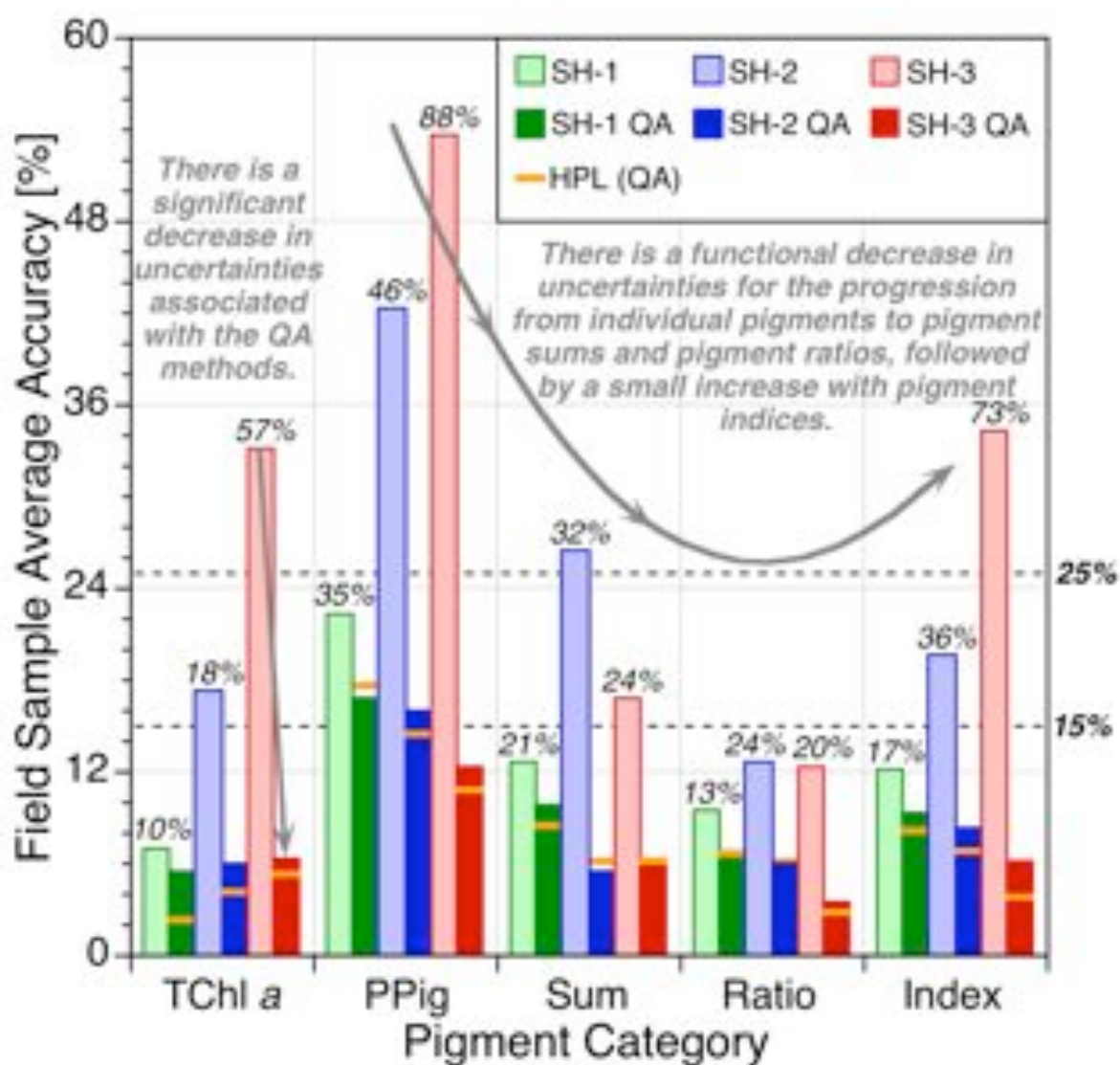
***Accuracy is telling a story truthfully, and precision is how similarly the story is repeated over and over again.***

Ultimately, what's needed are performance metrics to ensure validated methods are performing at the stated capabilities. In the absence of such information, a mixture of high quality to worst-case data are brought together and the artificially high variance associated with the substandard methods—which are not proper sources of truth—are shared by all the participants and biased results are obtained.



## Field Sample Uncertainties for the HPLC TChl *a* Concentration (Spanning 0.020 – 26.185 mg m<sup>-3</sup>)

The accuracy of the methods are primarily distinguished by the pigment categories and whether or not the methods were properly quality assured (dark bars) or not (light bars). For the latter, the worst-case average result is shown at the top of the bar (individual samples can be worse). **The QA methods have the lowest uncertainties**; they always meet the 25% validation requirement and almost always satisfy the 15% refinement objective. Furthermore, **there is a functional decrease in the uncertainties for the progression from the primary pigments to the sums and ratios, followed by a small increase with the indices.**

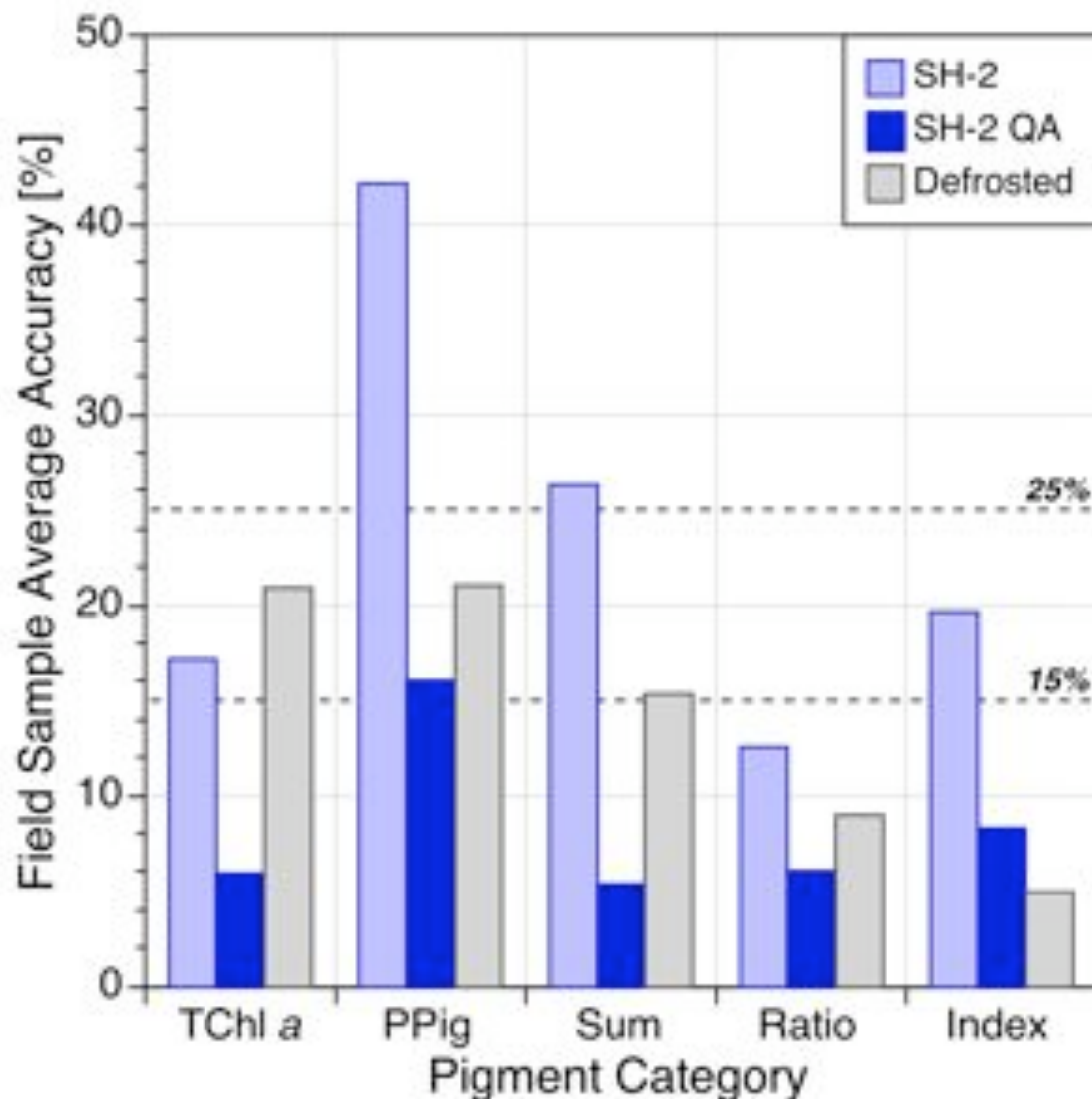






## The Primary Source of Uncertainty is Usually the Practitioners of the Methods

A recurring presumption in intercomparison experiments is *"Improper handling and storage of the field samples will overwhelm the uncertainty budget,"* that is, the variability from sample decay is much larger than the variability in the methods. This issue was addressed in SeaHARRE-2 by having one of the QA laboratories analyze a set of replicates unequivocally defrosted during shipping. The results showed *a quality-assured laboratory analyzing bad samples was superior to a method lacking a QA scheme and analyzing good samples.* This was confirmed by the precision data.







## SeaHARRE-4: Complex Coastal and Estuarine Waters Extending [TChl *a*] Close to 50 mg m<sup>-3</sup>

The emphasis for SeaHARRE-4 is on coastal and estuarine waters. The sample set includes 12 different sites from fjords, estuaries, and bays in Denmark. All samples were collected in triplicate and distributed after October 2006.



The sampling plan included a concerted effort to obtain the widest range in water properties possible (8 – 28 PSU) plus a diversity of phytoplankton populations (the maximum TChl *a* concentration is expected to exceed 40 mg m<sup>-3</sup>) to ensure a complex mix of pigments. *At some level, no one area is sufficient, but at another level, any one area is typical as long as the range in complexity of the coastal environment is captured.*



## SeaHARRE-4 Participants and Analysis

The laboratories represented in SeaHARRE-4 are a mixture of established and new HPLC practitioners as well as round-robin participants. The new additions (USC, FIO, GSFC, and Dalhousie) have well-established expertise in coastal sampling. Every effort was made to increase the diversity of international groups (e.g., a concerted effort was made to include a South American institute) and methods (e.g., the Zapata method), but the timing of the activity was not necessarily advantageous to the invitees. **All the participants agreed to make one or more additional analyses with the HPLC extracts to ensure a more comprehensive use of the samples.**

Sample Set	Institute or Laboratory	Principal Investigator	Country	Lab. Code	HPLC Pigs	Fluor. Chl a	Spec. Chl a	Absorption	Method
1	CSIRO	L. Clementson	Australia	C	H		S	A	Van Heukelem and Thomas
2	DHI	L. Schlüter	Denmark	D	H	F	S		Van Heukelem and Thomas
3	GSFC/UMBC	M. Russ	USA	G	H		S	A	Van Heukelem and Thomas
4	HPL	L. Van Heukelem	USA	H	H		S		Van Heukelem and Thomas
5	HPL			H'	H	F		A	Van Heukelem and Thomas
6	JRC	J-F. Berthon	Italy	J	H		S		Van Heukelem and Thomas
7	LOV	H. Claustre	France	L	H		S	A	Van Heukelem and Thomas
8	LOV			L'	H	F	S		Van Heukelem and Thomas
9	USC	J. Pinckney	USA	U	H	F	S		Pinckney
10	FIO	D. Millie	USA	F	H	F	S		Millie
11	SDSU/CHORS	C. Trees	USA	S	H	F			Wright et al.
12	Dalhousie Univ.	C. Normandeau	Canada	N	H	F			Wright et al.
12	10	10	6	12	12	7	9	4	4





## The HPLC Wall or, *What do you do When You Reach the Innermost Layer of the Onion?*

The primary pigments (TChl *a*, TChl *b*, TChl *c*, Caro, Allo, But-fuco, Diad, Diato, Fuco, Hex-fuco, Peri, and Zea) are comprised of 18 individual pigments (plus allomers and epimers). The calibration—*and traceability*—of these 18 pigments is based on the absorption coefficients of pigment extracts. The following pigments have absorption coefficients with an accuracy at the highest level of confidence, because the purity was checked using nuclear magnetic resonance (NMR):

*fucoxanthin, diatoxanthin, trans-neoxanthin, and 9'-cis-neoxanthin.*

Note the small number of pigments and the absence of any of the chlorophylls. In addition, the majority of the work done in determining absorption coefficients was executed in the 1960s, with diminishing contributions in the 1970s and 1980s; the oldest work dates to the 1930s. NMR was not available until after 1985.

For SeaHARRE-2 (the most comprehensive HPLC round robin so far), 76% of the results had a mismatch (of unknown magnitude) between the solvent system and the absorption coefficients (which are a function of the solvent system). The level of disagreement ranges from less than 1% (Chl *a*) to 25% (Diato) or more (DVChl *b*).

Solving this problem should include traceability to the mole, so the absorption coefficient becomes a *working standard* (of sorts) for transferring traceability (rather than the de facto standard, as it is now). This will be a topic in the next HPLC workshop (currently scheduled for the week of 22 October 2007 at DHI).





## The Legacy Instruments for Measuring the Apparent Optical Properties (AOPs) of Seawater



The capability for collecting high-quality AOP data in seawater has been advanced by investigating specific aspects of the observational problem set with incremental changes to the state of the art, both for above- and in-water systems. In terms of the Advanced Science Plan and the need for coastal measurements, the in-water legacy systems are not always well suited for properly resolving the optical complexity of shallow waters (principally because of the overall instrument size, proximity to the sampling platform, or the rate of descent). *Above-water systems—although already demonstrated to be very capable in coastal waters—do not provide any information about the vertical properties of the water column.* The needed advancement for in-water coastal sampling is considered next, again from the practical perspective of executing the work incrementally.





## Practical Advancements in AOP Instruments to Improve Observations in Shallow (Coastal) Waters

Free-fall profilers are needed to avoid platform (ship shadow) perturbations. Most are rocket-shaped devices, but **recent advances have tested the performance characteristics of kite-shaped profilers using existing sensor technology.**

*Flotation*

*19-channel (3.5in)  
Radiance Sensor*

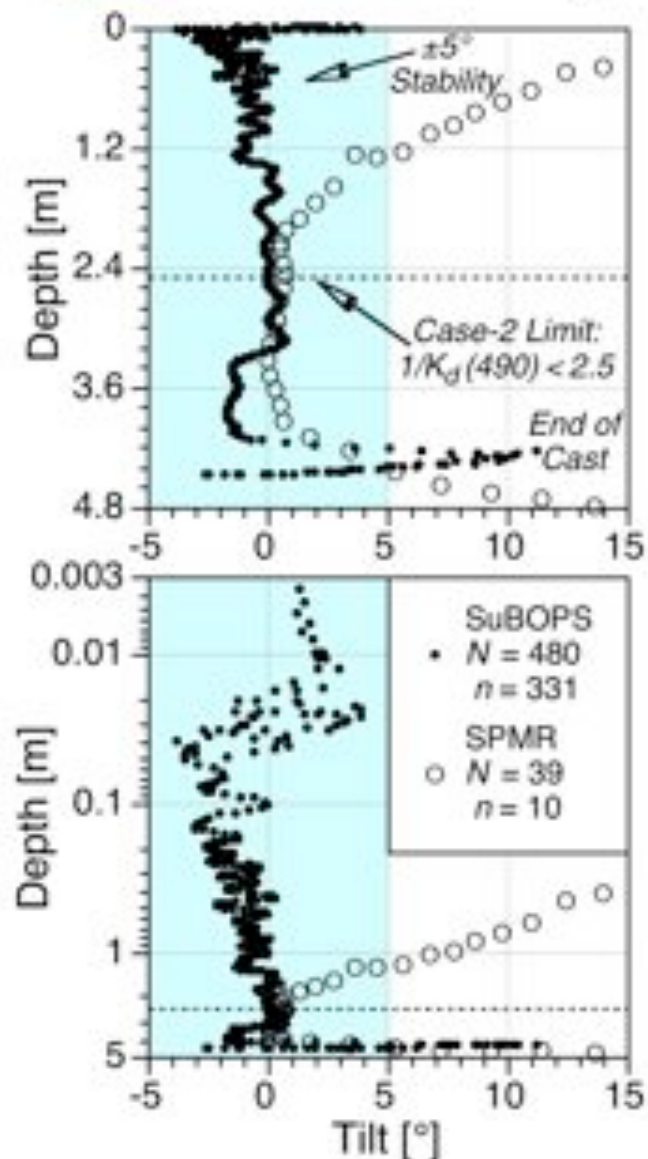
*19-channel (3.5in)  
Irradiance Sensor  
(plus pressure, 2-axis  
tilts, and temperature)*

The Submersible Biospherical Optical Profiling System (SuBOPS) is based on the current PRR series of radiometers which have **a spectral coverage of 320–865 nm**. The profiler is about **15 in H and 20 in W**.



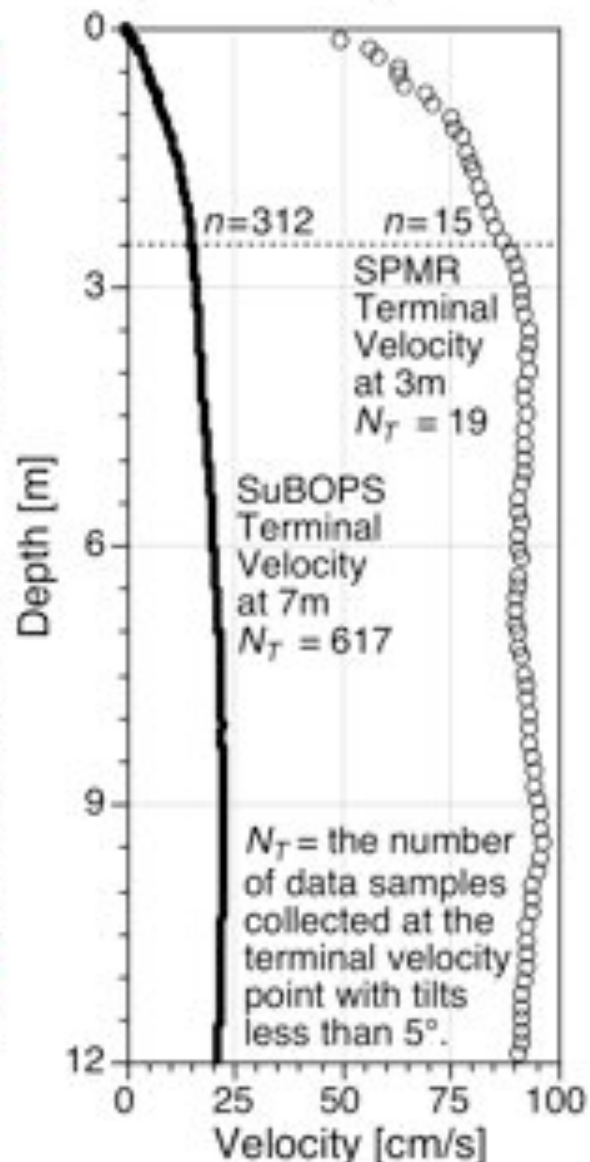


## Field Commissioning Results of the SuBOPS Prototype (PRR Sensors in 3.5 in Cylinders)



The emphasis on near-shore processes in the **Advanced Science Plan** requires an **unprecedented ability to collect high-quality data in shallow, optically-complex waters**. For design purposes, the latter is parameterized as a Case-2 limit:  $1/K_d(490) < 2.5$  m.

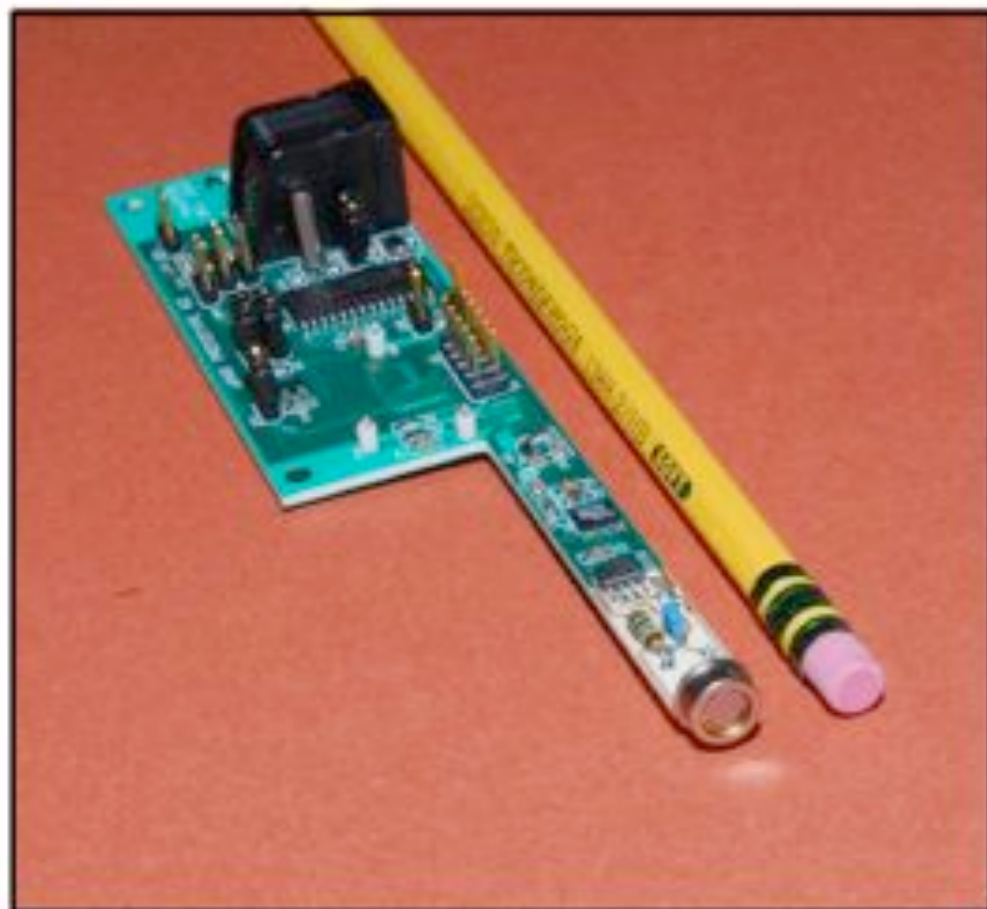
The design objectives are to maximize the number of samples a) for an entire profile,  $N$ ; b) within the top 2.5 m,  $n$ ; and c) between the surface and the depth of terminal velocity,  $N_T$ . The latter is used to establish a vertical resolution estimate for a profiler: **1.1 cm for SuBOPS** and 15.8 cm for the SPMR (3.5 in cylinder).



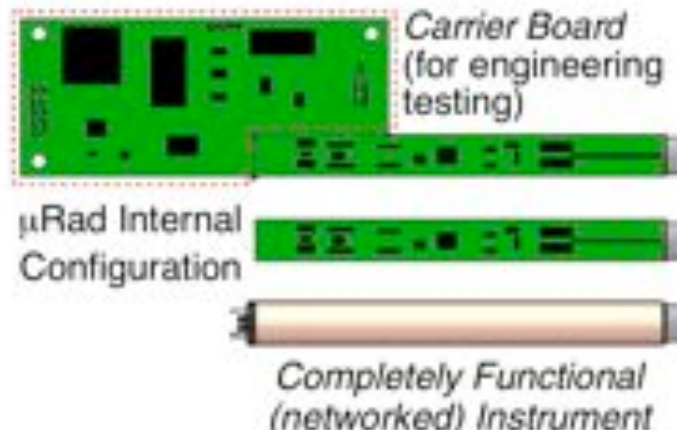




## The Miniaturization of AOP Sensors: The Development of the Micro-Radiometer Detector System



*A prototype (hand-made) micro-radiometer (0.355 in by 3.75 in) with attached carrier board. The latter is needed, because the circuitry of the former is so small, engineering and test data are not easily accessed with standard instrument probes.*



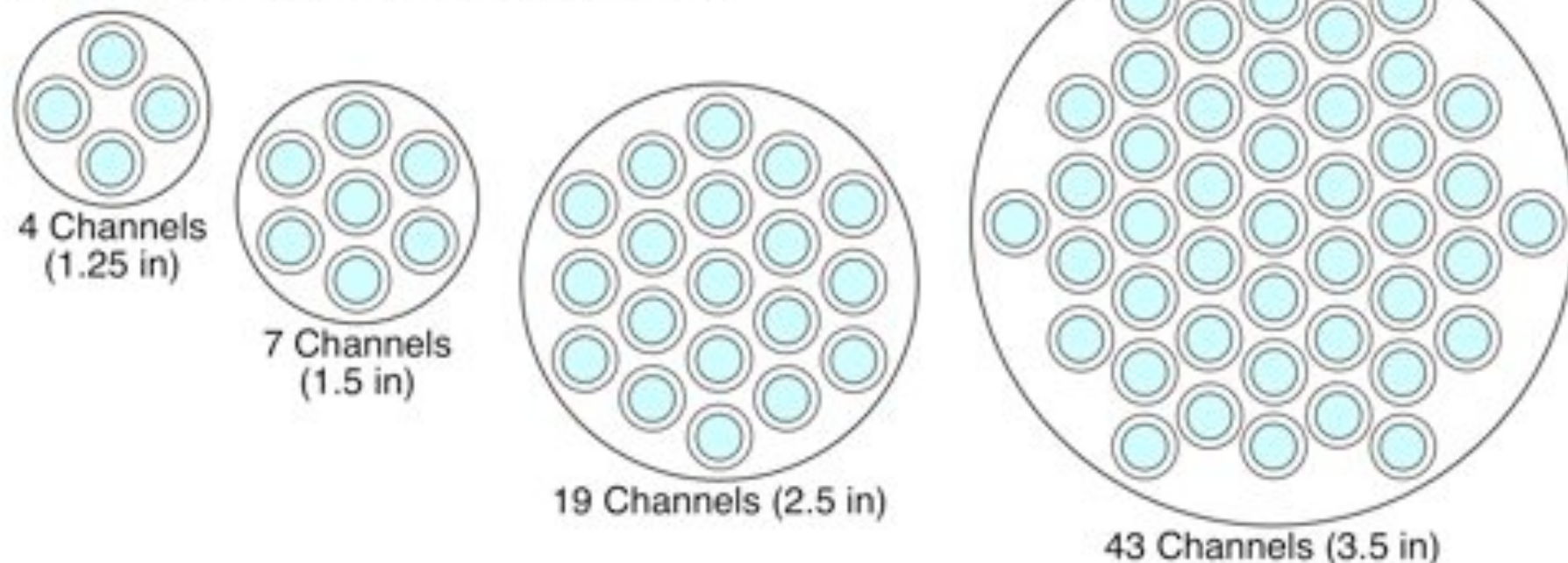
A 1-channel irradiance sensor will be about 0.75 in by 8.0 in (a little shorter for radiance). **The micro-radiometer specifications are:**

- Hamamatsu S1226-44BQ silicon photodiode (same as SuBOPS),
- **7 decades of dynamic range** (SuBOPS is 9),
- **3.5 mA per channel** (5.5 mA for SuBOPS), and
- **20 Hz data sampling rate for two 19-channel sensors** (SuBOPS is 12 Hz).



## Packing Factors and the Construction of Spectrally Expansive Sensors

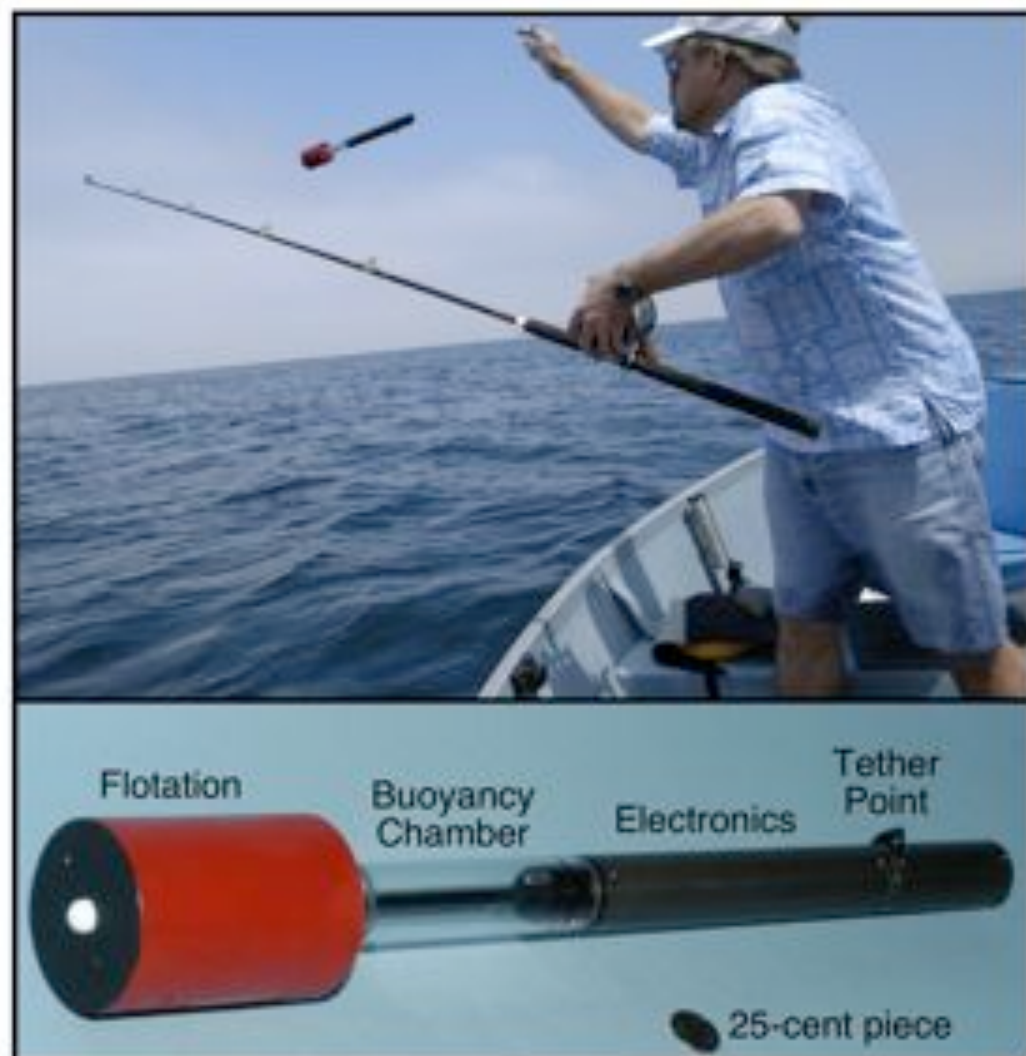
Each micro-radiometer is a completely functional (networked) instrument. Larger sensors will be constructed by clustering individual sensors in larger diameter housings (irradiance sensors, however, will have a single diffuser). Multiple sensors are controlled by an *aggregator*. Presently, 64 micro-radiometers can be controlled by one aggregator (which is potentially expandable to as many as 255 micro-radiometers), and 9 aggregators can be used within each sensor system. The packing factors involved produce the following example scenarios for instrument sizes (SuBOPS, which is a 19-channel instrument, is based on a 3.5 in pressure housing):







## Application of the Micro-Radiometers to a New AOP Deployment System: *The Castaway*



Although micro-radiometers are well suited for a variety of new applications (e.g., gliders, autonomous vehicles, balloons, etc.), **the original concept was to produce a new and easily deployed system for small-boat operations in shallow waters.** The deployment scenario is as follows:

- Throw or cast the tethered profiler away from the boat,
- **The impact (splash) dissipates as a buoyancy chamber slowly fills with seawater,**
- The profiler begins to sink very slowly (**based on the hole size in the buoyancy chamber**), and
- Once the buoyancy chamber is completely flooded, the profiler accelerates to the terminal velocity.



## Keeping all the Scientific Disciplines and Methodologies Synchronized to Similar Performance Levels



*This IOP frame is about 1 m tall and 0.5 m on each side and weighs about 40 kg. It contains an ac-9, ac-s, bb-9, two fluorometers, a fast CTD, a PAR sensor, two pumps, four flow meters, plus a data handling unit and all the requisite plumbing, valves, and filters.*

As one discipline advances (e.g., AOP sensors), this usually unbalances the paradigm, so it will be necessary to make sure opportunities are provided to the other disciplines to restore a balanced approach. This will be accomplished by first determining where the advancements are needed (new instruments, revised protocols, etc.), and then agreeing on the best way to fund the new work. If a substantial investment is needed (e.g., new sensors), either new funding sources will have to be identified or an incremental approach will have to be pursued (as was done very often during SeaWiFS). The new AOP instrument capability was accomplished with incremental and SBIR funding.





## Vicarious Calibration Alternatives From Measurements Satisfying *The Ocean Optics Protocols*

A timely and relevant example of how programmatic changes can be handled incrementally is will demonstrated by how the vicarious calibration requirement has been investigated in terms of what might be executed in the future. There has been a number of incremental technical accomplishments—most of which have been already shown to satisfy *The Ocean Optics Protocols*—that are being evaluated as sources of vicarious calibration data. Only one of these alternatives was funded explicitly to be vicarious calibration source, but they all offer the opportunity of reviewing how this important job is done without—*perhaps*—having to make a significant investment.

<b>Data Set</b> <b>(Lw Derivation)</b>		<b>Resolution</b>		<b>Sensors</b>		<b>Deployment</b>		<b>Other</b>
		<b>Vertical</b>	<b>Spectral</b>	<b>Source</b>	<b>Charact.</b>	<b>Environment</b>	<b>Mechanism</b>	<b>Considerations</b>
MOBY	Lu	Limited	Hyper	Custom	Extensive	Restricted	Autonomous	Bio-fouling; shading
NOMAD	Lu	Profiles	Multi	COTS	Limited	Constrained	Mostly Free-fall	Diverse data sources
SCAPA	Lu	Profiles	Multi	COTS	Moderate	Constrained	Mostly Free-fall	Opportunistic sampling
BOUSSOLE	Lu	Limited	Multi	COTS	Moderate	Constrained	Autonomous	Bio-fouling
OR Model	TChl a	None	Hyper	None	N/A	Case-1	Filter Sample	Many assumptions
Reflectance	Eu	Profiles	Multi	COTS	Limited	Constrained	Mostly Free-fall	"Global" Q-factor
SeaPRISM	LT	None	Multi	COTS	Limited	Variable	Autonomous	Not simultaneous
SIMBAD	LT	None	Multi	Custom	Limited	Constrained	Hand-Held	Opportunistic sampling

The above- and in-water methods are shown in yellow and blue, respectively. The OR Model is the Optical Reflectance Model (Morel and Maritorena 2001).